

Vertex functions, spectral weights, and anisotropy in phonon-assisted multimagnon optical absorption

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We discuss the general vertex function coupling light with phonon-assisted multimagnon excitations in perovskitelike antiferromagnets. We make a symmetry analysis and use exact diagonalization of a multiband Peierls-Hubbard Hamiltonian in a small cluster to propose a simple parametrization of the vertex. The parameters obtained determine the strength of the spectral weight, the optical anisotropy, and the momentum dependence of the vertex. The nonperturbative results are compared with perturbation theories in the hybridization. We find that although the momentum dependence of the vertex is similar to the one obtained in perturbation the absolute values renormalize strongly and the anisotropy in lamellar compounds changes in two orders of magnitude. This explains the success of the perturbative computation in getting the correct line shape for phonon-assisted multimagnon absorption [J. Lorenzana and G. A. Sawatzky, *Phys. Rev. Lett.* **74**, 1867 (1995)] but the poor results for the strength of the optical anisotropy. Our calculated values of the anisotropy are in good agreement with experiments. [S0163-1829(98)04236-2]

I. INTRODUCTION

Antiferromagnetic insulators show optical absorption bands related to spin excitations inside the insulating gap.¹⁻⁵ Recently, a detailed theory was presented that explained these bands in terms of phonon-assisted absorption of multimagnon excitations.⁶⁻⁸

These absorption bands reveal precious information about the dynamical response of the antiferromagnet that is difficult or impossible to obtain by other means like Raman or neutron scattering.⁹ In order to extract this information from the experiments a precise knowledge of the light-magnon-phonon vertex function is needed.

Previous studies⁶⁻⁸ have used perturbation theory in the hybridization (PTH) to derive an effective Hamiltonian for the coupling of light with these excitations. However, real materials are far from being in the perturbative regime.¹⁰ Despite that, computations using PTH give an excellent account of the experimental line shapes.⁶⁻⁸

On the other hand, a striking feature of the experimental data in layered materials is the very strong optical anisotropy of these absorption bands. For example, in materials with CuO₂ layers almost all the spectral weight appears when the electric field is oriented in the CuO₂ planes (see Fig. 1). This is puzzling for the theory because no selection rule precludes to have an absorption perpendicular to the plane. In fact, PTH strongly underestimate the optical anisotropy.

In this work we present a nonperturbative method to compute the vertex functions based on exact diagonalization of a multiband Peierls-Hubbard Hamiltonian on a small cluster. We find that the overall scale of the vertex function determining the spectral weight gets strongly renormalized in covalent systems like the cuprates. This can change the optical anisotropy in as much as two orders of magnitude respect to the PTH result. This is in good agreement with the very strong anisotropy observed.

In addition, the general symmetry properties of the vertex are discussed. This allows us to propose a simple parametrization of the vertex. We find that the momentum dependence

of the vertex is quite similar to the one obtained with PTH. This explains the success of PTH to describe the *line shapes* and put those theoretical results on firmer grounds.

We also study the effect of the direct exchange between the metal and the ligand in perovskitelike materials that is necessary to describe correctly¹¹ the magnetic coupling between metals. We find that for some parameters the momentum dependence of the vertex changes qualitatively giving access to different regions in momentum space.

The paper is organized as follow. In Sec. II we make a brief outline of the theory and discuss the symmetries of the vertex. Then we compare the results obtained for the anisotropy in PTH (Sec. III) vs the nonperturbative approach (Sec. IV). Finally we present our conclusions (Sec. V).

II. MULTIMAGNON INFRARED ABSORPTION

A. Model

Here we present a brief account of the theory to fix the notation. For details see Ref. 7. For simplicity we refer to an insulating CuO₂ plane (spin-1/2, one hole per Cu) but similar arguments apply to other antiferromagnets with larger spin or different dimensionality.

The theory starts from a multiband Peierls-Hubbard Hamiltonian in the presence of an electrical field \mathbf{E} :

$$\begin{aligned}
 H = & \sum_{i \neq j, \sigma} t_{ij}(\{\mathbf{u}_k\}) c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i, \sigma} e_i(\{\mathbf{u}_k\}, \mathbf{E}) c_{i\sigma}^\dagger c_{i\sigma} \\
 & + \sum_i U_i c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger c_{i\downarrow} c_{i\uparrow} + \sum_{i \neq j, \sigma, \sigma'} U_{ij} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j\sigma'} c_{i\sigma} \\
 & + \sum_{i \neq j, \sigma, \sigma'} K_{ij} c_{i\sigma}^\dagger c_{j\sigma'}^\dagger c_{j\sigma} c_{i\sigma'} + \sum_l \frac{\mathbf{p}_l^2}{2M_l} \\
 & + \sum_{k,l} \frac{1}{2} \mathbf{u}_k \bar{\mathbf{k}}_l \mathbf{u}_l - \mathbf{E} \cdot \mathbf{P}_{ph}, \quad (1)
 \end{aligned}$$

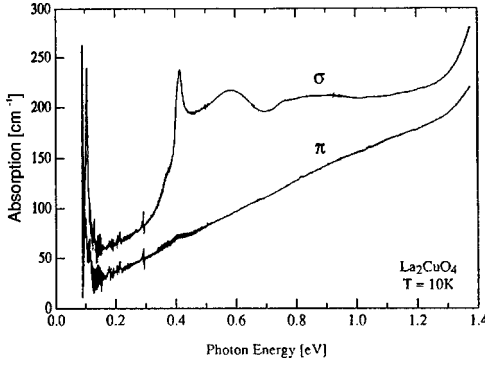


FIG. 1. Measured absorption with the electric field parallel (σ) and perpendicular (π) to the CuO_2 plane for La_2CuO_4 as a function of the photon energy (Ref. 2). A linear background must be subtracted from the experimental data that almost agree with the π absorption.

where the $c_{i\sigma}^\dagger$ operator creates a hole at orbital i (we consider Cu $d_{x^2-y^2}$ and O $p_{x,y}$ orbitals).

For the on-site matrix elements we take $e_i = E_{d,i}(E_{p,i})$ and $U_i = U_d(U_p)$ for i in a Cu (O) site. For the intersite Coulomb matrix elements we take $U_{ij} = U_{pd}$ (direct) and $K_{ij} = K_{pd}$ (exchange) if i and j are Cu and O nearest neighbors, and zero otherwise. K_{pd} , the exchange integral between Cu and O (Ref. 11) was not included in Ref. 7 and it is necessary to get the correct value of the superexchange for the accepted values of the other parameters.¹⁰ t_{ij} is the hopping between nearest neighbors ($t_{pd,ij}$, between Cu and O; $t_{pp,ij}$ between two oxygens).

M_l is the mass of the atoms, \mathbf{p}_l is their momentum, \mathbf{u}_i is the displacement from the equilibrium position \mathbf{R}_i , and $\bar{\mathbf{k}}_{kl}$ is a spring constant tensor. \mathbf{P}_{ph} is the phonon dipole moment. For simplicity we only allow the O to move. With this approximation $\mathbf{P}_{ph} = eZ\sum_k \mathbf{u}_k$, and Z is the ionic charge of the O ($Z = -2$).

The on-site energies and the hoppings are modified with the movement of the atoms¹² and with the electric field according to:

$$\begin{aligned} t_{pd,kl}(\{\mathbf{u}_k\}) &= t_{pd}^0 + (\pm)\alpha \frac{(\mathbf{R}_k - \mathbf{R}_l)}{|\mathbf{R}_k - \mathbf{R}_l|} \mathbf{u}_k \\ t_{pp,kl}(\{\mathbf{u}_k\}) &= t_{pp}^0 + (\pm)\gamma \frac{(\mathbf{R}_k - \mathbf{R}_l)}{|\mathbf{R}_k - \mathbf{R}_l|} (\mathbf{u}_k - \mathbf{u}_l) \\ E_{d,i}(\{\mathbf{u}_k\}, \mathbf{E}) &= E_d^0 + \beta \sum_k' (\mp) \mathbf{u}_k \cdot e\mathbf{E} \cdot (\mathbf{R}_i + \mathbf{u}_i) \\ E_{p,i}(\{\mathbf{u}_k\}, \mathbf{E}) &= E_p^0 + e\mathbf{E} \cdot (\mathbf{R}_i + \mathbf{u}_i). \end{aligned} \quad (2)$$

For the hopping ($t_{pp,kl}$, $t_{pd,kl}$) the sign in parenthesis is such that the matrix element increases if the atoms came closer. With the on-site energy $E_{d,i}$ (or $E_{p,i}$) the opposite is true. The prime in the sum in k indicates nearest neighbors.

From now on we will reserve latin index i, j, k to label Cu sites, greek index α, β to label the Cu-Cu bonds and also the O's that site on those bonds, and greek indexes μ, ν to label the Cartesian components of the vectors. In two-dimensional (2D) systems we take a coordinate system with the x axis in

the direction of a Cu-O bond and the z axis perpendicular to the Cu-O plane. With this convention $\alpha, \beta = x, y$ in two-dimensional systems. For systems with 1D Cu-O chains we will take x as the chain direction.

We will take the following reference parameter sets appropriated for Cu-O planes (all energy values in eV)^{7,12,13} and chains:

$$U_p = 5; \quad U_d = 8; \quad U_{pd} = 1$$

$$t_{pp}^0 = 0.5; \quad t_{pd}^0 = 1.2$$

$$\alpha = \frac{7}{2} \frac{t_{pd}^0}{a_{pd}}; \quad \beta = 2 \frac{U_{pd}}{a_{pd}}; \quad \gamma = \sqrt{2} \frac{t_{pp}^0}{a_{pd}}$$

$$a_{pd} = 3.6 \text{ a.u.}$$

To study the effect of covalency $\Delta \equiv E_p^0 - E_d^0$ is taken variable in the range 0–10. For K_{pd} we took two values: $K_{pd} = 0$ and $K_{pd} = -0.22$.

B. Effective Hamiltonian and optical conductivity

At low energies all physical properties are given by a Heisenberg-like Hamiltonian for the layer:

$$H = \sum_{i,\alpha} J_{i,\alpha}(\{\mathbf{u}_k, \beta\}, \mathbf{E}) B_{i,\alpha} + H_{ph} - \mathbf{E} \cdot \mathbf{P}_{ph}. \quad (3)$$

Here, $B_{i,\alpha} = \mathbf{S}(\mathbf{R}_i) \mathbf{S}(\mathbf{R}_i + \mathbf{e}_\alpha)$ where $\mathbf{R}_i + \mathbf{e}_\alpha$ is the position of the Cu nearest neighbor of site i in α direction. $J_{i,\alpha}(\{\mathbf{u}_k, \beta\}, \mathbf{E})$ is a generalized superexchange depending on the phonons and electric field. It will be computed in the following sections by two different methods.

$J_{i,\alpha}$ can be expanded as a Taylor series in \mathbf{E} and $\{\mathbf{u}_k, \beta\}$. For a given Cu-Cu bond like the one in Fig. 2 this reads

$$\begin{aligned} J_{i,\alpha} &= J_0 + \sum_\nu \frac{\partial J_{i,\alpha}}{\partial E^\nu} E^\nu + \sum_{j,\beta,\mu} \frac{\partial J_{i,\alpha}}{\partial u_{j,\beta}^\mu} u_{j,\beta}^\mu \\ &+ \sum_{j,\beta,\mu,\nu} \frac{\partial^2 J_{i,\alpha}}{\partial E^\nu \partial u_{j,\beta}^\mu} E^\nu u_{j,\beta}^\mu + \dots \end{aligned} \quad (4)$$

J_0 is the usual superexchange. $\partial J_{i,\alpha} / \partial E^\nu$ is zero because of symmetry. This means that there is not direct absorption of magnons (See Ref. 7).

The 1st order derivatives in \mathbf{u} [Eq. (4)] gives the magnon-phonon interaction. Second order derivatives in \mathbf{u} renormalize the spring constants $\bar{\mathbf{k}}$ or give higher order magnon-phonon interactions. All of these terms are discussed in Ref. 7 and will not be discussed here.

The second-order cross-derivatives in \mathbf{E} and \mathbf{u} are the terms responsible for the coupling of the electric field with the magnon and phonons and are the ones that we analyze in detail in this work.

We define

$$q_{\alpha\beta}^{\mu\nu}(\mathbf{R}_{i,\alpha} - \mathbf{R}_{j,\beta}) \equiv \frac{\partial^2 J_{i,\alpha}}{\partial E^\nu \partial u_{j,\beta}^\mu}. \quad (5)$$

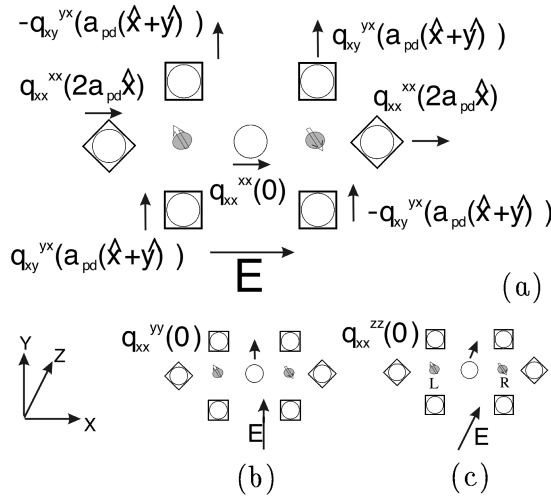


FIG. 2. (a), (b), and (c) Different charges when the electric field is in the x, y, z directions, respectively. Only the non-negligibly charges are shown. In the case of the electric field in the x direction we also show the sign of the charges. The thicker arrows represent the Cu holes. R and L identify the right and left Cu.

$q_{\alpha\beta}^{\mu\nu}(\mathbf{R}_{i,\alpha} - \mathbf{R}_{j,\beta})$ has units of charge so we call it an effective charge for the coupling of light with magnon-phonon excitations.

We introduce the Fourier transforms:

$$B_{i,\alpha} = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_i} B_{\mathbf{k},\alpha}. \quad (6)$$

$$u_{i,\beta}^{\mu} = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}_i} u_{\mathbf{k},\beta}^{\mu}. \quad (7)$$

$$q_{\alpha\beta}^{\mu\nu}(\mathbf{R}_{i,\alpha} - \mathbf{R}_{j,\beta}) = \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)} q_{\alpha\beta}^{\mu\nu}(\mathbf{k}). \quad (8)$$

The dipole moment can be computed as $\mathbf{P} = -\nabla_{\mathbf{E}} H$. Using Eqs. (3)–(8) one gets

$$\mathbf{P} = \mathbf{P}_{1ph} + \mathbf{P}_{2ph} + \mathbf{P}_{1ph+mag} + \dots \quad (9)$$

\mathbf{P}_{1ph} and \mathbf{P}_{2ph} are the dipole moment related to the absorption of one and two phonons, respectively, and will not be considered here (see Ref. 7). $\mathbf{P}_{1ph+mag}$ is associated with the absorption of magnons assisted by a one-phonon process:

$$P_{1ph+mag}^{\nu} = -N^2 \sum_{\mathbf{p}, \alpha, \beta, \mu} q_{\alpha\beta}^{\mu\nu}(\mathbf{p}) B_{-\mathbf{p}\alpha} u_{\mathbf{p}\beta}^{\mu}. \quad (10)$$

Once $q_{\alpha\beta}^{\mu\nu}(\mathbf{p})$ is known we can compute the optical conductivity. From the dipole-dipole correlation function we get for ν polarization:⁷

$$\sigma^{\nu}(\omega) = \omega \sigma_0 \sum_{\mathbf{p}, \alpha', \alpha} q_{\mathbf{p}, \alpha', \alpha}^2 \text{Im} \langle \langle B_{\mathbf{p}}^{\alpha'}; B_{-\mathbf{p}}^{\alpha} \rangle \rangle (\omega - \omega_0). \quad (11)$$

Here we use Zubarev's notation¹⁴ for the Green's function $\langle \langle B_{\mathbf{p}}^{\alpha}; B_{-\mathbf{p}}^{\alpha'} \rangle \rangle$, ω_0 is the phonon frequency that we assumed

to be independent of momentum and phonon polarization and defined the light-magnon-phonon vertex as

$$q_{\mathbf{p}, \alpha', \alpha, \nu}^2 \equiv \frac{N^2}{e^2} \sum_{\beta, \mu} q_{\alpha\beta}^{\mu\nu}(\mathbf{p}) q_{\alpha'\beta}^{\mu\nu}(-\mathbf{p}), \quad (12)$$

$$\sigma_0 = -\frac{4\pi e^2}{MV_{cu}\omega_0}. \quad (13)$$

V_{cu} is the volume per Cu atom.

We define the optical anisotropy θ as

$$\theta = \frac{\int \sigma^x(\omega) d\omega}{\int \sigma^z(\omega) d\omega}. \quad (14)$$

C. Symmetry considerations and parametrization of the vertex

Here we discuss the general symmetry of the vertex. This will greatly simplify the computations below.

Since the vertex is given by derivatives of J , and J is associated with a Cu-Cu bond the relevant symmetry group is the one that leaves the lattice invariant respect to point group operations centered *in the bond* (i.e., an O site). In our case this is \mathbf{D}_{2h} .

In Eq. (5) \mathbf{E} and \mathbf{u} transform as vectors so the second order derivatives transforms as the product of their transformations. It is easy to check that the vertex transform like irreducible representations of \mathbf{D}_{2h} .¹⁵ With this $q_{\alpha\beta}^{xx} = \partial^2 J / \partial E^x \partial u^x$ transforms as the $\mathbf{A}_g(x^2)$ representation, $q_{\alpha\beta}^{xy} = \partial^2 J / \partial E^x \partial u^y$ as $\mathbf{B}_{1g}(xy)$, $q_{\alpha\beta}^{xz} = \partial^2 J / \partial E^x \partial u^z$ as the $\mathbf{B}_{2g}(xz)$ representation, etc. This fixes all the relative signs of the charges as displayed in Fig. 2.

Apart from being related by symmetry, for reasonable parameters the charges decreased quickly with the distance between the bond and the O that moves $[\mathbf{R}_{i,\alpha} - \mathbf{R}_{j,\beta}]$ in Eq. (5)]. This allows us to describe all the non-negligible and nonsymmetrically related charges with only four parameters:

$$q_{\alpha\alpha}^{zz}(0) = q_I$$

$$q_{\alpha\alpha}^{\beta\beta}(0) = q_I^*$$

$$q_{\alpha\alpha}^{\alpha\alpha}(0) = q_{A2}$$

$$q_{\alpha\alpha}^{\alpha\alpha}(2a_{pd}\hat{x}) = -q_A$$

$$q_{\alpha\beta}^{\beta\alpha}[a_{pd}(\hat{x} + \hat{y})] = -q_A, \quad (15)$$

where $\alpha \neq \beta$. The last relation holds only approximately. With our parameters the difference is less than 10%.

In the next sections we will compute these parameters with two different methods.

With this parametrization the vertex functions [Eq. (12)] for a Cu-O plane takes the form

$$q_{\mathbf{p}, \alpha, \alpha}^2 = q_{A2}^2 - 4q_{A2}q_A \cos(p_\alpha) + 4q_A^2 \cos^2(p_\alpha) + 16q_A^2 \sin^2\left(\frac{p_\alpha}{2}\right) \sin^2\left(\frac{p_\beta}{2}\right) \quad (16)$$

$$q_{\mathbf{p},\alpha,\alpha,\beta}^2 = q_I^{*2} \quad (17)$$

$$q_{\mathbf{p},\alpha,\alpha,z}^2 = q_I^2. \quad (18)$$

Here $\alpha \neq \beta$. The rest of the $q_{\mathbf{p}}^2$ are zero or negligible. For a Cu-O chain in the x direction like the ones in Sr_2CuO_3 the vertex takes the form

$$q_{\mathbf{p},x,x,x}^2 = q_{A2}^2 - 4q_{A2}q_A \cos(p_x) + 4q_A^2 \cos^2(p_x) \quad (19)$$

$$q_{\mathbf{p},x,x,y}^2 = q_I^2 \quad (20)$$

$$q_{\mathbf{p},x,x,z}^2 = q_I^2 \quad (21)$$

and as previously, the rest of the $q_{\mathbf{p}}^2$ are zero or negligible.

III. PERTURBATIVE COMPUTATION OF THE EFFECTIVE CHARGES

J can be computed for a general configuration of the oxygens and the electric field using perturbation at the 4th order in the hopping t_{pd} (Ref. 10) as the splitting between the singlet and the triplet state. For simplicity we will consider the Cu_2O_7 cluster shown in Fig 2. This is an exact 4th order computation when K_{pd} , $t_{pp}=0$ and a very good approximation otherwise. In the former case we get

$$J^{(4)} = 2t_R^2 t_L^2 \left[\frac{1}{\epsilon} \left(\frac{1}{\Delta_L} + \frac{1}{\Delta_R} \right)^2 + \frac{1}{\Delta_L^2} \frac{1}{U_d + (\Delta_L - \Delta_R)} + \frac{1}{\Delta_R^2} \frac{1}{U_d - (\Delta_L - \Delta_R)} \right], \quad (22)$$

where we defined

$$\Delta_L \equiv (\Delta + U_{pd}) - e a_{pd} \hat{\mathbf{x}} \mathbf{E} - e \mathbf{u}_{0,x} \mathbf{E} + \lambda \beta \sum_{k,\alpha} (\pm) u_{k,\alpha}^\alpha$$

$$\Delta_R \equiv (\Delta + U_{pd}) + e a_{pd} \hat{\mathbf{x}} \mathbf{E} - e \mathbf{u}_{0,x} \mathbf{E} - \lambda \beta \sum_{k,\alpha} (\pm) u_{k,\alpha}^\alpha$$

$$\epsilon \equiv (2\Delta + U_p) - 2e \mathbf{u}_{0,x} \mathbf{E} + \lambda \beta \sum_{k,\alpha} (\pm) u_{k,\alpha}^\alpha$$

$$t_R \equiv t_{pd} + \alpha \mathbf{u}_{0,x}$$

$$t_L \equiv t_{pd} - \alpha \mathbf{u}_{0,x}.$$

The sum in k is over nearest neighbors and a_{pd} is the distance between Cu and O.

As noted by other authors¹¹ it is important to include in the Hamiltonian K_{pd} to get a correct estimate of J . For example, for $K_{pd} = -0.22$ and $\Delta = 2.7$ eV we get, using exact diagonalization, (see next section) $J_0 = 0.13$ eV which is the accepted value of the superexchange for La_2CuO_4 . Although K_{pd} is relatively small it has a strong effect because it enters in second order¹⁰ as

$$J^{(2)} = 2K_{pd} \left(\frac{t_L^2}{\Delta_L^2 - K_{pd}^2} + \frac{t_R^2}{\Delta_R^2 - K_{pd}^2} \right). \quad (23)$$

With these expressions one can compute all the derivatives in Eq. (4). This gives access to the magnon-phonon interaction, effective charges, and all other possible coupling between magnons, phonons, and light.

Making a power expansion when K_{pd} , t_{pd} , βa_{pd} , and αa_{pd} are much smaller than Δ_0 , U_d , and U_p we get the following parameters:

$$q_I = 8e \frac{t_{pd}^4}{\Delta^2} \left[\frac{1}{\Delta_0} \left(\frac{1}{U_d} + \frac{2}{\epsilon_0} \right) + \frac{2}{\epsilon_0^2} \right] + 8e \frac{t_{pd}^2}{\Delta^3} K_{pd}$$

$$q_A = 8e \frac{t_{pd}^4}{\Delta^2} \beta a_{pd} \left[\frac{2}{\Delta_0^2} \left(\frac{1}{U_d} + \frac{2}{\epsilon_0} \right) + \frac{1}{U_d} \left(\frac{1}{\Delta_0} + \frac{2}{U_d} \right)^2 \right] + 24e \frac{t_{pd}^2}{\Delta^4} \beta a_{pd} K_{pd}$$

$$q_{A2} = -2q_A + q_I + q_C$$

$$q_I^* = q_I,$$

where we defined

$$\epsilon_0 = 2\Delta + U_p$$

$$\Delta_0 = \Delta + U_{pd}$$

$$q_C = -16e \frac{t_{pd}}{\Delta^3} \alpha a_{pd} K_{pd}.$$

We see that only 3 parameters are independent and when $K_{pd}=0$ only 2.

In Fig. 3 we show the charges as a function of Δ . The mechanism giving rise to q_I and q_A in the absence of K_{pd} were discussed in Ref. 7. q_I is due to the process in which the charge of the O that moves depends on the surrounding spin configuration. We call it a local charge. On the other hand, q_A is related to a process in which the displacement of an O produces a spin depend flow of charge between copers, reminiscent of the charge-phonon effect.¹⁶ We call it a nonlocal charge.

Due to the fact that K_{pd} appears at lower order in the perturbations theory it gives a strong contribution to the effective charges, and the contribution q_C appears. This last charge can be understood in the following way: When the central O moves in the bond direction t_L and t_R , and Δ_L and Δ_R in Eq. (23) get out of balance producing a spin dependent flow of charge, i.e., q_C is a nonlocal charge.

IV. NONPERTURBATIVE COMPUTATION OF THE EFFECTIVE CHARGES AND SPECTRAL WEIGHTS

To obtain nonperturbative values for $q_{\alpha\beta}^{\mu\nu}(\mathbf{R}_i)$ we compute exactly J using a Lanczos exact diagonalization technique¹⁷ taking the full Peierls-Hubbard Hamiltonian [Eq. (1)]. $J(\{\mathbf{u}_{k\alpha}\}, \mathbf{E})$ is obtained as the splitting between the singlet ground state and the first excited triplet state in a Cu_2O_7

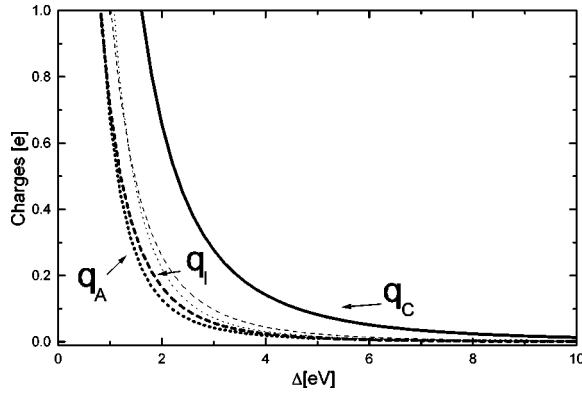


FIG. 3. Perturbative charges q_A (dotted lines), q_I (dashed lines), and q_C (full line) as a function of Δ for the parameters of Sec. II. The thick lines correspond to $K_{pd} = -0.22$ and the thin lines to $K_{pd} = 0$. In this last case $q_C = 0$ (not shown).

cluster for a general configuration of $\{\mathbf{u}_{i\alpha}\}$ and \mathbf{E} . Then the derivatives in Eq. (4) are obtained numerically. For the matrix element values given in Sec. II all 4 parameters in Eq. (15) are needed.

In Fig. 4 we show the charges obtained with exact diagonalization and perturbations. As expected for the big Δ both computations converge (see inset). However, this convergence is extremely slow, much slower than for the superexchange (see Ref. 10). This makes perturbation theory a very poor approximation to determine the charges.

We see that the charges q_I , q_I^* , and q_C are overestimated in perturbations while q_A is underestimated. Notice that in PTH q_I and q_A are of the same order whereas in the exact computation they differ strongly. This has dramatic consequences for the optical anisotropy as we show below. Also q_C , which in perturbation is entirely due to K_{pd} , is strongly overestimated in that approach.

For q_A this can be understood on the basis that this is a dynamical process where, associated with the displacement of the O's, there is a flux of charge from one Cu to the other. There are processes beyond fourth order perturbation theory that are very important for this charge. For example, one

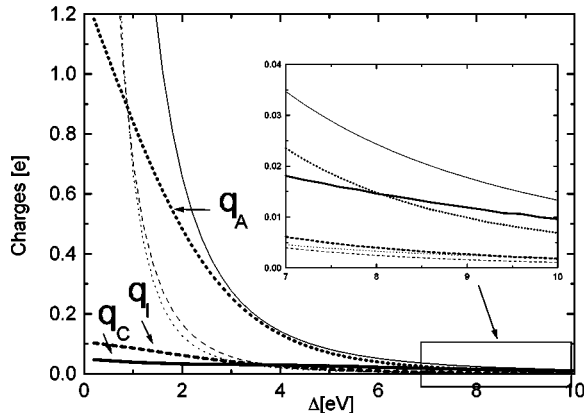


FIG. 4. Charges q_A (dotted lines), q_I (dashed lines), and q_C (full line) as a function of Δ for the parameters of Sec. II and $K_{pd} = -0.22$. The thick curves correspond to the exact computation and the thin ones to the perturbative result. The insets show an expansion of the large Δ region.

process that becomes important in covalent systems and is not taken into account in perturbations at the considered order is the jump of one hole from one Cu to the O's surrounding the other and forming a Zhang-Rice singlet in the final state.¹⁸ Clearly, this kind of process is of a larger order in perturbation than the one considered above. We believe that this process makes q_A dominate over the other charges for covalent materials.

From the above results we conclude that the vertex strongly simplifies in a planar covalent material as

$$q_{\mathbf{p},\alpha,\alpha,\alpha}^2 = 16q_A^2 \left[\sin^2\left(\frac{p_\alpha}{2}\right) \sin^2\left(\frac{p_\beta}{2}\right) + \sin^4\left(\frac{p_\alpha}{2}\right) \right], \quad (24)$$

$$q_{\mathbf{p},\alpha,\alpha,\beta}^2 = q_I^2, \quad (25)$$

$$q_{\mathbf{p},\alpha,\alpha,z}^2 = q_I^2. \quad (26)$$

Here, $\alpha \neq \beta$. The rest of the $q_{\mathbf{p}}^2$ are zero or negligible. We see that q_A determines the strength of the in-plane absorption, whereas q_I determines the out-of-plane absorption.

Equation (24) is the same expression proposed on Refs. 6 and 7 on heuristic arguments and which we put here on firmer grounds. We see that the in-plane vertex filters out the $\mathbf{p}=0$ response.

For covalent systems with Cu-O chains we get:

$$q_{\mathbf{p},x,x,x}^2 = 16q_A^2 \sin^4\left(\frac{p_x}{2}\right), \quad (27)$$

$$q_{\mathbf{p},x,x,y}^2 = q_I^2, \quad (28)$$

$$q_{\mathbf{p},x,x,z}^2 = q_I^2. \quad (29)$$

This is the form used in Ref. 8 to describe the absorption in Sr_2CuO_3 .

A quick estimate of the spectral weights in the 2D case neglecting quantum fluctuations in the ground state (see the Appendix) shows that the anisotropy goes like this:

$$\theta \approx 5 \left(\frac{q_A}{q_I} \right)^2. \quad (30)$$

From this quadratic dependence and from the previous results for the charges we can see that PTH will give a very poor result for the optical anisotropy.

In Fig. 5 we see the optical anisotropy computed by diagonalizing exactly the Heisenberg model on a 4×4 lattice. We have exactly evaluated $\langle\langle B_{\mathbf{p}}^y; B_{-\mathbf{p}}^y \rangle\rangle$ in Eq. (11) and computed the optical anisotropy both with the exact charges and the perturbative ones. We see that the exact estimate differs from the perturbative one in two order of magnitudes. This explains the strong anisotropy seen in the experiments and that cannot be explained in a perturbative computation.

It is interesting to remark that for very ionic materials q_C dominates. In this limit the in-plane vertex becomes momentum independent ($q_{\mathbf{p},\alpha,\alpha,\alpha}^2 = q_C^2$) giving access to the whole momentum space.

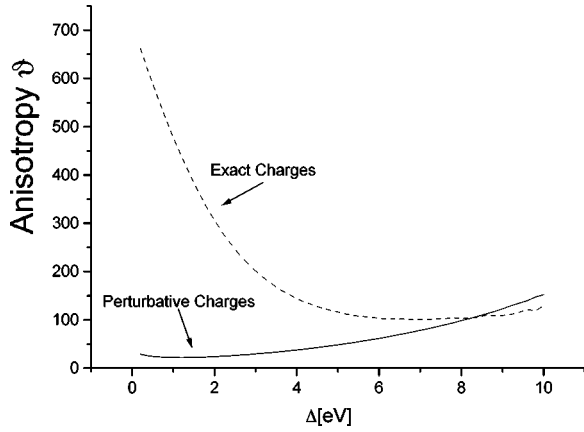


FIG. 5. Optical anisotropy as a function of Δ calculated with $K_{pd} = -0.22$ and the parameters of Sec. II. We used the perturbative charges and the exact ones.

V. CONCLUSIONS

We have shown that PTH is a very poor approximation to compute the strength of phonon-assisted multimagnon absorption bands in covalent materials. We introduced a non-perturbative method based on exact diagonalization of a small cluster. With the latter we find that the overall strength gets strongly renormalized respect to the former method depending on the electric field polarization. For electric fields in the plane we find a much larger strength, whereas for electric fields perpendicular to the plane we find a much lower spectral weight. As a result we find an enormous optical anisotropy that is in accord with the experimental result (Fig. 1).

On the contrary, the momentum dependence of the vertex

is in good accord with the one used in Refs. 6–8. This explains the success of these works to describe the first peak of the two magnon-phonon assisted excitations in the planar compound La_2CuO_4 ^{6,7} and the whole spectrum in the 1D compound Sr_2CuO_3 .⁸

Additionally, we discussed the symmetry of the vertex. This fixes the way the vertex transforms under the different symmetry operation and should serve as a guide to find simple parametrizations or to get a semiphenomenological one when it is difficult or impossible to get the charges.

We generalized the theory for a more realistic Hamiltonian than the one considered previously,⁷ including the direct Cu-O exchange. We find a contribution to the vertex that dominates for very ionic materials and that makes the vertex practically momentum-independent, giving access to the whole Brillouin zone.

APPENDIX: ISING ESTIMATES OF SPECTRAL WEIGHT

Here we present a quick estimate of the spectral weights when the quantum fluctuations of the ground state are neglected. This provides us with simple expressions for the spectral weights.

We neglect the xy part of the operators in the Hamiltonian but keep it in the dipole moment operator \mathbf{P} [Eq. (10)]. Since the ground state is now the classical Neel state and there are not quantum fluctuations, it is trivial to compute the dynamical correlation function of Eq. (11),

$$\text{Im}\langle\langle B_{\mathbf{p}}^{\alpha}; B_{-\mathbf{p}}^{\beta} \rangle\rangle_{\text{Neel}}^{\omega_0} = \frac{1}{4} \delta(\omega - 3J - \omega_0), \quad (\text{A1})$$

and to get an analytical expression for the anisotropy.

¹R. Newman and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

²J. D. Perkins, J. M. Graybeal, M. A. Kastner, R. J. Birgeneau, J. P. Falck, and M. Greven, Phys. Rev. Lett. **71**, 1621 (1993).

³J. D. Perkins, D. S. Kleinberg, M. A. Kastner, R. J. Birgeneau, Y. Endoh, K. Yamada, and S. Hosoya, Phys. Rev. B **52**, R9863 (1995).

⁴J. D. Perkins, Ph.D. thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1994.

⁵H. Suzuura, H. Yasuhara, A. Furusaki, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. **76**, 2579 (1996).

⁶J. Lorenzana and G. A. Sawatzky, Phys. Rev. Lett. **74**, 1867 (1995).

⁷J. Lorenzana and G. A. Sawatzky, Phys. Rev. B **52**, 9576 (1995).

⁸J. Lorenzana and R. Eder, Phys. Rev. B **55**, R3358 (1997).

⁹E. Manousakis, Rev. Mod. Phys. **63**, 1 (1991).

¹⁰H. Eskes and J. H. Jefferson, Phys. Rev. B **48**, 9788 (1993).

¹¹E. B. Stechel and D. R. Jennison, Phys. Rev. B **38**, 4632 (1988).

¹²W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman, San Francisco, 1980).

¹³K. Yonemitsu, A. R. Bishop, and J. Lorenzana, Phys. Rev. B **47**, 12 059 (1993).

¹⁴D. N. Zubarev, Usp. Fiz. Nauk **71**, 71 (1960) [Sov. Phys. Usp. **3**, 320 (1960)].

¹⁵E. Wigner, *Group Theory* (Academic Press, London, 1959).

¹⁶M. J. Rice, Solid State Commun. **31**, 93 (1979).

¹⁷E. R. Gagliano and C. A. Balseiro, Phys. Rev. B **38**, 11 766 (1988).

¹⁸F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).